



ATTN: BOX PROVISIONAL PATENT APPLICATION
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In re Provisional Application of

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Provisional Application No.: 60/121,436

Filed: February 23, 1999

For: CARBON MATERIAL FOR LITHIUM BATTERY

SUBMISSION OF VERIFIED ENGLISH LANGUAGE TRANSLATION

BOX PROVISIONAL PATENT APPLICATION

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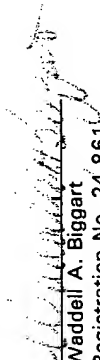
Sir:

In response to the "Notice to File Missing Parts of Provisional Application Filed Under 37 CFR 1.53(b)(2)", mailed March 22, 1999, submitted herewith is the verified English language translation (35 pages of specification) for the above-mentioned provisional application previously filed in the Japanese language.

A check for the statutory fee of \$130.00 is attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. 1.16 and 1.17 which may be required during the entire pendency of the provisional application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

The English language translation is being filed on Monday, May 24, 1999. Since the due date for filing this document fell on a Saturday, the filing of the document on May 24, 1999 is considered timely.

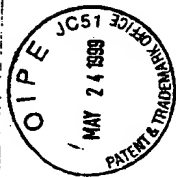
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APPLICATION NUMBER	FILING/RECEIPT DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO./TITLE
0252/0322	0252/0322	NOT ASSIGNED	00000

SUBJECT: FUJIN ZINN HADPEAK & SEAS
2100 PENNSYLVANIA AVENUE N.W.
WASHINGTON, DC 20007-1202

DATE MAILED: 03/22/99

NOTICE TO FILE MISSING PARTS OF PROVISIONAL APPLICATION
(Filed Under 37 CFR 1.53 (c))
Filing Date Granted

An Application Number and Filing Date have been assigned to this Provisional Application. The items indicated below, however, are missing. Applicant is given TWO MONTHS FROM THE DATE OF THIS NOTICE within which to file all required items and pay fees required below to avoid abandonment. Extensions of time may be obtained by filing a petition accompanied by the extension fee under the provisions of 37 CFR 1.136(e). If any of items 1 or 2 are indicated as missing, the SURCHARGE set forth in 37 CFR 1.18(f) of \$25.00 for a small entity in compliance with 37 CFR 1.27, or \$50.00 for a non-small entity, must also be timely submitted in reply to this NOTICE to avoid abandonment.

If all required items on this form are filed within the period set below, the total amount owed by applicant as a

☐ small entity (statement filed) ☐ non-small entity is \$ 130

☐ 1. The statutory provisional application filing fee is:

- ☐ missing.
☐ insufficient.

Applicant must submit \$ _____ to complete the basic filing fee and/or file a small entity statement claiming such status (37 CFR 1.27).

☐ 2. The provisional application cover sheet under 37 CFR 1.151(c)(1) is required identifying:

- ☐ either the city and state or city and foreign country of the residence of each inventor.
☐ the title of the invention.

☒ 3. The application was filed in a language other than English.

Applicant must file a verified English translation of the application, the \$130.00 set forth in 37 CFR 1.17(k), unless previously submitted, and a statement that the translation is accurate (37 CFR 1.52(d)).

☐ 4. A \$50.00 processing fee is required since your check was returned without payment (37 CFR 1.21 (m)).

☐ 5. Your filing receipt was mailed in error because your check was returned without payment.

☐ 6. The drawings contained in the application cannot be scanned or properly stored because they

- ☐ do not comply with the size requirements (8-1/2 by 11 inches or 21.0 by 29.7 cm).
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DECLARATION

I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/121,436 filed on February 23, 1999.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 20th day of May, 1999

Atsuko Ikeda
Atsuko Ikeda

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[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION]

Carbon Material for Lithium Battery

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A carbon material for a lithium battery, comprising graphite powder having a specific surface area of $3 \text{ m}^2/\text{g}$ or less, an aspect ratio of 6 or less and a tapping bulk density of 0.8 g/cm^3 or more.

[Claim 2] The carbon material for a lithium battery as claimed in claim 1, wherein the graphite powder has an average particle size of from 8 to $30 \text{ }\mu\text{m}$.

[Claim 3] The carbon material for a lithium battery as claimed in claim 1 or 2, wherein the graphite powder contains substantially no particle having a particle size of $3 \text{ }\mu\text{m}$ or less and/or $53 \text{ }\mu\text{m}$ or more.

[Claim 4] The carbon material for a lithium battery as claimed in claims 1 to 3, wherein the graphite powder has a Co value of 6.745 \AA or less.

[Claim 5] The carbon material for a lithium battery as claimed in claims 1 to 4, wherein the graphite powder contains boron.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a carbon material for

a lithium battery, more specifically, the present invention relates to a carbon material for a lithium battery having high discharge capacity, high charge and discharge efficiency and excellent cycle property.

[0002]

[Background Art]

In recent years, portable tools such as pocket telephone, compact video camera and note-type personal computer are making a remarkable development, and as a power source therefor, demands for a compact secondary battery such as Ni-hydrogen secondary battery or lithium secondary battery are increasing.

In particular, a nonaqueous solvent-type lithium battery using lithium which is the basest metal has a possibility that a compact lightweight high energy density battery can be realized. Accordingly, investigations and developments thereof are aggressively proceeding.

The lithium battery using metal lithium as a negative electrode is, however, disadvantageous in that dendritic acicular lithium crystals are readily generated and break through the separator to short-circuit and allow the inflammable solvent to catch fire, thus, firing accidents are liable to occur.

As an effective means for solving this problem, a lithium ion secondary battery using a carbonized or

graphitized carbon material for the negative electrode and a nonaqueous solvent containing lithium ion for the electrolytic solution has been proposed and is used in practice.

More specifically, the charge and discharge reaction is designed to take place in such a manner that when the carbon is doped, intercalated or the like acted by lithium ion, charging is assigned, whereas when the lithium ion is dedoped or deintercalated, discharging is assigned, so that the metal lithium can be prevented from precipitating and can be completely used. Studies on this reaction mechanism are aggressively proceeding but complete elucidation is not yet reached.

In the lithium secondary battery, a carbon material is used as the negative electrode, lithium is used as an active material thereof, a transition metal chalcogenide such as MnO_2 , V_2O_5 , FeS and TiS_2 , a composite oxide thereof with lithium, a Chevrel phase compound or an active carbon material is used as the positive electrode, and a nonaqueous organic solvent containing lithium ion is used as the electrolytic solution. Examples of the organic solvent include propylene carbonate, ethylene carbonate, methyl ethyl carbonate, 1,2-dimethoxyethane, 1,2-diethoxyethane, γ -butyrolactone and tetrahydrofuran. Specific examples of the electrolytic solution include LiClO_4 , LiAsF_6 ,

LiPF_6 , LiBF_4 , LiCH_3SO_3 , and LiCl .

[0003]

In order to elevate the discharge capacity of the lithium battery, the amount of lithium taken in into the carbon must be increased as much as possible. On the other hand, the lithium taken in must be easily released. These intake and release actions preferably proceed smoothly and do not cause any large change in the balance therebetween even if the actions are repeated. When this is successfully done, a high current efficiency and a long cycle life can be attained.

It is said that as the graphite has a higher crystallinity, the amount of lithium taken in into a carbon (graphite) material increases. In general, the graphite can have more improved crystallinity when the graphitization temperature is higher. However, the graphitization temperature is generally about $3,200^\circ\text{C}$ at the highest and there is a definite limit in improving the crystallization of graphite only by the temperature condition. In order to get out of this problem, JP-A-8-31422 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") discloses a technique of adding boron (B) to carbon powder and graphitizing the mixed powder, thereby elevating the crystallinity. Also, JP-A-9-259886 discloses a technique of processing a specific carbon to thereby

improve the crystallinity of graphite powder and reduce the specific area ratio.

In the lithium battery, graphite powder formed into a paste using a binder is coated on a metal mesh or the like to form an electrode (negative electrode). The powder used preferably has a small specific surface area. The reasons therefor are described below. A passivity film comprising an electrolytic solution or the like is formed on the surface of the graphite powder and as the specific surface area of the powder is larger, the production of passivity film increases. The passivity film is a great cause of the reduction in the use efficiency of lithium. Furthermore, the specific surface area being large means that the activity is high, accordingly, the electrolytic solution decomposes at a high reaction rate and the cycle life is shortened. Also, when the specific surface area of powder becomes large, the amount of binder used in the formation of powder into a poled plate increases and the coverage of binder on the graphite particle proportionally increases. As a result, the contact ratio between the graphite particle and the electrolytic solution is reduced and the charge and discharge capacity decreases.

[0004]

The method for obtaining graphite powder includes a method of pulverizing coke and the like and then

graphitizing the powder and a method of graphitizing coke and the like and then pulverizing them. JP-A-6-295725 employs the latter method but according to this method, the powder particle is flat and has a large aspect ratio, accordingly, the battery performance is low.

[0005]

[Problems to be Solved by the Invention]

The discharge capacity may be increased by elevating the crystallinity of graphite and reducing the specific surface area of graphite powder. However, not only these are participants but the permeability of electrolytic solution attributable to the shape of graphite powder or the filling ratio of graphite particles at the formation into an electrode also has an effect on the battery properties. In the patent publications described above, these problems are not dealt with specifically.

The object of the present invention is to provide a carbon material for a lithium battery, ensuring large discharge capacity, high charge and discharge efficiency, excellent cycle property, good coating performance and increase in the carbon density in the electrode, in which the carbon powder is graphitized after the properties thereof are previously controlled.

[0006]

[Means to Solve the Problems]

The present invention has been accomplished as a result of investigations to solve the above-described problems and comprises the following inventions.

(1) A carbon material for a lithium battery, comprising graphite powder having a specific surface area of $3 \text{ m}^2/\text{g}$ or less, an aspect ratio of 6 or less and a tapping bulk density of 0.8 g/cm^3 or more.

(2) The carbon material for a lithium battery as described in (1) above, wherein the graphite powder has an average particle size of from 8 to $30 \text{ }\mu\text{m}$.

(3) The carbon material for a lithium battery as described in (1) or (2) above, wherein the graphite powder contains substantially no particle having a particle size of $3 \text{ }\mu\text{m}$ or less and/or $53 \text{ }\mu\text{m}$ or more.

(4) The carbon material for a lithium battery as described in (1) to (3) above, wherein the graphite powder has a Co value of 6.745 \AA or less.

(5) The carbon material for a lithium battery as described in (1) to (4) above, wherein the graphite powder contains boron.

[0007]

[Mode for Carrying Out the Invention]

The present invention is the above-described carbon

material for a lithium battery, comprising graphite carbon. This carbon material is particularly suitable as the negative electrode of a lithium battery. The graphite powder preferably has good crystallinity as much as possible and in the graphite structure where hexagonal net face layers are stacked, the lattice spacing (Co) is 6.745 Å or less, preferably 6.730 Å or less, more preferably 6.720 Å or less.

The graphite powder of the present invention may contain a graphitization catalyst such as boron (B), beryllium, aluminum or silicon. Among these, boron is effective. When B is added to carbon powder and the powder is graphitized, the graphitization degree (degree of crystallinity) elevates and a small Co value is obtained. Furthermore, if the crystallinity is the same, a lower processing temperature can be used in the graphitization by adding B as compared with the case of not adding B. The content of B may be in the range of allowing solid solution of B within the graphite crystal. Even if the B content exceeds this range, the effect as a catalyst does not increase any more. The upper limit is about 10 wt%. In other words, the graphite powder of the present invention may contain B in an amount of about 10 wt% or less, preferably 5 wt% or less.

[0008]

The specific surface area of the graphite powder as the electrode of a lithium battery is preferably smaller. The graphite powder for use in the present invention has a specific surface area (BET method) of $3 \text{ m}^2/\text{g}$ or less. If the specific surface area exceeds $3 \text{ m}^2/\text{g}$, the surface activity of the graphite powder is elevated and due to the decomposition of electrolytic solution or the like, the Coulomb efficiency decreases. Furthermore, a large amount of binder is required in the formation of electrode, which gives rise to high coverage of binder on the graphite particle and in turn reduction in the discharge capacity of the battery fabricated. In addition, as described above, if the activity is enhanced, the surface of graphite particle enters the passive state and the performance is liable to decrease. Important factors for reducing the specific surface area are the particle size, the particle shape, the particle size distribution, the surface property and the like. In particular, the graphite particle is preferably formed into a nearly spherical shape.

In order to increase the capacity of a battery, it is important to raise the filling density of graphite particles. Also to this purpose, the graphite powder particle preferably has a nearly spherical shape but not a scaly shape. If this particle shape is expressed by an

aspect ratio, the graphite powder particle for use in the present invention has an aspect ratio of 6 or less, preferably 5 or less. The aspect ratio is generally the (length of long axis)/(length of short axis) ratio of a particle and the value thereof may be obtained from a microphotograph of the particle, however, in the present invention, the aspect ratio is determined as follows.

An average particle size A calculated by the laser diffraction scattering method and an average particle size B calculated by the electrical detection method (Coulter•Counter method) are obtained. From principles of respective measurements, A is recognized as the diameter of a sphere corresponding to the largest length of the particle and B is recognized as the diameter of a sphere having the same volume as the particle. Assuming that the particle is a disk, the bottom face diameter of disk is A, the volume is $4/3 \times (B/2)^3 \pi = C$ and then, the thickness of disk can be calculated by $T = C / (A/2)^2 \pi$. Accordingly, the aspect ratio is A/T.

In general, when the graphite is pulverized, the resulting particle is liable to have a scaly shape in many cases. In particular, when graphite is first formed and then pulverized, the higher the processing temperature, the stronger the tendency of forming scaly particles and moreover, the smaller the particle size of the powder, the

more liable the formation of scaly particles. The electrode plate of a battery is formed by coating a paste containing graphite powder on a metal mesh or metal sheet such as aluminum and then press-bonding it. At this time, if the aspect ratio of graphite powder exceeds 6, the scaly graphite particles are oriented to readily form a mirror surface. If a mirror face is formed, the permeability of electrolytic solution into the electrode plate is deteriorated and the discharge capacity of battery decreases. Furthermore, the scaly graphite is poor in the particle filling property and therefore reduces the bulk density.

[0009]

As the graphite powder which works out to the electrode of a lithium battery has a more satisfactory filling property, namely, a higher bulk density, the battery can have a higher discharge capacity. The graphite powder for use in the present invention has a tapping bulk density of 0.8 g/cm³ or more, preferably 0.9 g/cm³ or more.

In the present invention, the tapping bulk density is measured as follows.

A fixed amount of graphite powder (6.0 g) is weighed and placed in a 15-mm ϕ cell for measurement and the cell is set in a tapping apparatus. After the free dropping of 400 times from the height of 45 mm at a tapping rate of 2

sec/time, the volume is measured and from the relationship between the weight and the volume, the bulk density is calculated.

The tapping bulk density of graphite powder is related to the particle size, the shape and the surface properties of the particle, and varies according to the particle size distribution even with the same average particle size. If the number of scaly particles or fine particles is large, the tapping bulk density may not be elevated. For example, after merely pulverizing a graphite material to have an average particle size of from 10 to 30 μm , many fine particles are produced and a tapping bulk density of 0.8 g/cm^3 or more is very difficult to attain using the powder. The graphite powder for use in the present invention has a high tapping density and at the same time, has a small aspect ratio for the graphite powder, namely, is shaped not scaly or low in the level of scales, so that the electrolytic solution can permeate without any disturbance and the filling density can be elevated.

[0010]

The graphite powder for use in the present invention preferably has a particle size in terms of the average particle size of from 8 to 30 μm , more preferably from 10 to 25 μm . This average particle size is determined by the laser diffraction scattering method, more specifically,

using an apparatus Macrotrack HRA manufactured by Nikkiso KK. The measuring conditions are such that 50 mg of a sample is weighed and added to 50 ml of distilled water, 0.2 ml of a 2% aqueous Triton (surface active agent) solution is further added thereto, the mixed solution is ultrasonic dispersed for 3 minutes and then, the average particle size is determined by the apparatus.

If the average particle size of graphite powder is less than 8 μm , not only a large aspect ratio is liable to result but also the specific surface area is increased and difficultly controlled to a value of 3 m^2/g or less specified in the present invention and also the tapping bulk density of powder is not elevated. As a result, the voltage flatness becomes bad and this is disadvantageous in fabricating a battery. The voltage flatness means a flatness of the charge and discharge curve. More specifically, in the case of a battery where a metal Li is used as a standard electrode and Li is intercalated/deintercalated into the carbon electrode, the charge and discharge curve has a long continuing plateau region in the vicinity of 100 mV. This part is preferably small in the voltage change and long continues and this is an index for the flatness. The capacity of the battery is a sum of this plateau region and the subsequent trapping region where adsorption/desorption of Li to the particle

surface takes place involving an abrupt increase in the voltage. The trapping region increases as the surface area of particle becomes larger, as a result, the flatness decreases. The decrease in the flatness comes out as the voltage fluctuation when the electrode is loaded into a battery and in the case of an apparatus where stable voltage is required, disadvantageously narrows the usable region and causes reduction in the capacity.

In forming an electrode using graphite powder, a method of forming the graphite powder into a paste with a binder and coating the paste on a metal plate or the like is generally used. If the average particle size of the powder is less than 8 μm , this means that fine powder particles having a particle size of less than 8 μm are contained in a fairly large amount, and the paste suffers from increased viscosity and poor coatability. Therefore, also in this point of view, the average particle size of the powder is preferably 8 μm or more. It is more preferred to remove particles having a particle size of less than 8 μm by classification or the like.

[0011]

The upper limit of the particle size of graphite powder is restricted by the fact that the thickness of the graphite powder layer formed of the above-described paste is usually from 50 to 200 μm . In order to uniformly

distribute graphite particles as much as possible, the average particle size of graphite powder is preferably 30 μm or less. If coarse particles having a particle size of 53 μm or more are mixed in the graphite powder, many irregularities are generated on the electrode surface and give rise to damage of the separator used in the battery.

From these aspects, the graphite powder of the present invention preferably has an average particle size of from 8 to 30 μm . The graphite powder more preferably contains substantially no (5 wt% or less) particle having a particle size of 3 μm or less and/or no particle having a particle size of 53 μm or more by removing those particles. When particles having a particle size of 3 μm or less or 53 μm or more are removed, the average particle size of graphite powder is from 10 to 25 μm .

[0012]

The graphite powder of the present invention can be produced as follows.

In order to obtain graphite powder, coke is usually first produced. The raw material of coke is petroleum pitch or coal pitch and by carbonizing the raw material, coke is produced. For forming graphite powder from coke, a method of pulverizing coke and then graphitizing the particles, a method of graphitizing the coke itself and then pulverizing it, a method of adding a binder to coke, molding and

calcining the mixture, graphitizing the calcined product (coke and this calcined product are collectively called coke and the like) and then pulverizing it into powder is usually used.

However, when the coke and the like are graphitized and then pulverized, scaly powder is likely produced because crystals are grown. Therefore, in order to obtain powder particles having a small aspect ratio, namely, close to sphere as much as possible for use in the present invention, it is preferred to pulverize coke and the like before graphitization, classify the particles into predetermined particle size and specific surface area, and then graphitize the particles. The raw material coke and the like preferably have no grown crystal, accordingly, those heat-treated at 2,000°C or less, preferably 1,200°C or less are suitably used.

The aspect ratio varies depending on the kind of raw material coke. Coke is known to include easily graphitizable coke, so-called needle coke, and non-needle coke having graphitizability inferior to the needle coke. According to the knowledge of the present inventors, it has been found that when coke is pulverized into powder, non-needle coke is suitable for obtaining powder particles having a small aspect ratio, namely, nearly spherical particles. Therefore, the raw material coke is preferably

non-needle coke heat-treated at 2,000°C or less, preferably 1,200°C or less.

[0013]

When the powder of coke and the like is graphitized, not only crystallization proceeds but also the surface area of the particle is reduced, thus, the above-described method is preferred also in this point. For example, the coke powder having an average particle size of about 10 μm obtained by pulverizing coke has a specific surface area of about 14 m^2/g . When this powder is graphitized at 2,800°C or more, the specific surface area is reduced to from 2 to 3 m^2/g . On the other hand, if the coke is graphitized and then pulverized, the specific area is at least 5 m^2/g or more and in some cases, 10 m^2/g or more, though it may vary according to the particle size. It is considered that in the method of pulverizing coke and then graphitizing particles, the carbon atoms are re-oriented at the graphitization and furthermore, a part of the surface evaporates due to high-temperature processing, therefore, the surface is cleaned or smoothed and thereby the specific area is reduced.

For pulverizing the coke and the like, a high-speed rotation pulverizer (e.g., hammer mill, pin mill, cage mill), a ball mill of various types (e.g., rolling mill, vibrating mill, planetary mill), a stirring mill (e.g.,

beads mill, attritor, circulating tube-type mill, annular mill) or the like may be used. Furthermore, a screw mill, turbo-mill, supermicron mill or jet mill or a pulverizer may also be used by selecting the conditions.

The coke and the like are pulverized by means of such a pulverizer and at this time, the average particle size is preferably adjusted to from 8 to 30 μm by selecting the pulverization conditions and if desired, classifying the powder. More preferably, particles having a particle size of 3 μm or less and/or particles having a particle size of 53 μm or more are substantially removed to reduce the amount of the particles in respective particle sizes to 5 wt% or less, preferably 1 wt% or less. When particles having a particle size of 3 μm or less and particles having a particle size of 53 μm or more are removed, the resulting particles have an average particle size of from 10 to 25 μm .

[0014]

The classification of coke powder and the like may be performed by any method as far as the particles can be separated. For example, a sieve classification method or an air classifier such as forced vortex-type centrifugal classifier (e.g., micron separator, turbo-plex, turbo-classifier, superseparator) or inertial classifier (e.g., modified virtual impactor, elbow jet) may be used. Furthermore, a wet sedimentation or centrifugal

classification method may also be used.

The temperature at the graphitization of coke and the like powder is preferably higher, however, there is a limit by an apparatus or the like. Accordingly, the graphitization temperature is preferably 2,500 to 3,200°C. The graphitization may be performed by a method of using an Acheson furnace where coke and the like powder is placed in a graphite crucible and electricity is passed directly therethrough, or a method of heating the powder by a graphite heating element.

In the case of incorporating boron (B) into the graphite powder, a boron source such as B single element, H_3BO_3 , B_2O_3 , B_4C and BN is added to the coke and the like powder, well mixed and then graphitized. If the B compound is non-uniformly mixed, the product itself is disproportionated and moreover, the compound is highly probably sintered at the graphitization. The amount of B added is small, therefore, the boron source is preferably formed into powder having a particle size of 50 μm or less, preferably 20 μm or less before mixing it with the coke and the like powder. The boron in the graphite powder is sufficient if it is contained in an amount of 10 wt% or less. Therefore, the amount of the boron source added to coke and the like is set such that the graphite powder after graphitization has a B element content of 10 wt% or

less.

[0015]

The specific surface area of graphite powder can be adjusted to 3 m²/g or less by the above-described control of average particle size, removal of fine particles, graphitization of coke powder after pulverization or the combination thereof.

A small aspect ratio of graphite powder particle can be obtained by pulverizing coke and the like before graphitization, where the crystals are not fully grown, and thereby reducing scaly particles. The aspect ratio may be increased by removing fine particles having a particle size of 3 μm or less. In this way, the aspect ratio of graphite powder can be adjusted to 6 or less, preferably 5 or less.

The bulk density of graphite powder is higher as the aspect ratio is smaller. On the other hand, the bulk density decreases as fine particles having a small particle size are increased. Even with the same average particle size, the bulk density varies depending on the particle size distribution of powder. When the graphite material is pulverized and then graphitized, the surface is smoothed simultaneously with the progress of crystallization and unevenness is reduced. By this method, the bulk density is increased.

Using such controlling of the aspect ratio and the

average particle size and adjustment of the particle size distribution by classification or the like, the tapping bulk density is increased to 0.8 g/cm³ or more, preferably 0.9 g/cm³ or more.

[0016]

[Examples]

The present invention is described in greater detail below by referring to the Examples and Comparative Examples.

The cokes used in the Examples and Comparative Examples are LPC-S coke produced by Shin Nittetsu Kagaku as non-needle coke (calcined product) (hereinafter referred to as Coke A) and LPC-UL coke produced by the same company as a needle coke (calcined product) (hereinafter referred to as Coke B). In respective Examples and Comparative Examples, 30 kg of the coke was used for the test.

[0017]

Example 1:

Coke A was coarsely pulverized in a pulverizer (manufactured by Hosokawamicon) into a size of from 2 to 3 mm or less. This coarsely pulverized product was finely pulverized in a jet mill (IDS2UR, manufactured by Nippon Neumatic). At this time, 96% (% means wt%, hereinafter the same) of coarse particles having a particle size of 35 μ m or more were continuously removed. The powder particles were air-classified in a turbo-classifier (TC15N,

manufactured by Nisshin Engineering) to remove 98% of particles having a particle size of 3 μm or less. At this time, the average aspect ratio was 4.0. A part of this pulverized product (15 kg) were sealed into a graphite crucible with a cover having an internal diameter of 40 cm and a volume of 40 ℓ , the crucible was placed in an Acheson furnace and the powder was graphitized at a temperature of 2,800°C. The powder was left standing to cool and taken out to obtain 14 kg of powder. This powder was passed through a 270 mesh (53 μm) according to ASTM Standard to remove particles having a particle size of 53 μm or more which were slightly produced due to coagulation at the graphitization. The properties of the graphite powder obtained are shown in Table 1.

[0018]

Example 2:

Coke A was coarsely pulverized in a pulverizer (manufactured by Hosokawamicon) into a size of from 2 to 3 mm or less. This coarsely pulverized product was finely pulverized in a jet mill (IDS2UR, manufactured by Nippon Neumatic). At this time, 95% of coarse particles having a particle size of 50 μm or more were continuously removed. The powder particles were air-classified in a turbo-classifier (TC15N, manufactured by Nisshin Engineering) to remove 98% of particles having a particle size of 8 μm or

less. At this time, the average aspect ratio was 3.9. A part of this pulverized product (15 kg) were sealed into a graphite crucible with a cover having an internal diameter of 40 cm and a volume of 40 l, the crucible was placed in an Acheson furnace and the powder was graphitized at a temperature of 2,800°C. The powder was left standing to cool and taken out to obtain 14 kg of powder. This powder was passed through a 270 mesh (53 μ m) according to ASTM Standard to remove particles having a particle size of 53 μ m or more. The properties of the graphite powder obtained are shown in Table 1.

[0019]

Example 3:

Coke A was coarsely pulverized in a pulverizer (manufactured by Hosokawamicron) into a size of from 2 to 3 mm or less. This coarsely pulverized product was finely pulverized in a jet mill (IDS2UR, manufactured by Nippon Neumatic). At this time, 95% of coarse particles having a particle size of 50 μ m or more were continuously removed. The powder particles were air-classified in a turbo-classifier (TC15N, manufactured by Nisshin Engineering) to remove 98% of particles having a particle size of 8 μ m or less. At this time, the average aspect ratio was 4.0. To a part of this pulverized product (14.4 kg), 0.6 kg of boron carbide (B_4C) was added and mixed in a Henschel mixer at 800.

rpm for 5 minutes. The mixture powder was sealed into a graphite crucible with a cover having an internal diameter of 40 cm and a volume of 40 l, the crucible was placed in an Acheson furnace and the powder was graphitized at a temperature of 2,800°C. The powder was left standing to cool and taken out to obtain 14 kg of powder. This powder was passed through a 270 mesh (53 µm) according to ASTM Standard to remove particles having a particle size of 53 µm or more. The properties of the graphite powder obtained are shown in Table 1.

[0020]

Example 4:

Coke A was coarsely pulverized in a pulverizer (manufactured by Hosokawamicron) into a size of from 2 to 3 mm or less. This coarsely pulverized product was finely pulverized in a jet mill (IDS2UR, manufactured by Nippon Neumatic). At this time, 95% of coarse particles having a particle size of 50 µm or more were continuously removed. At this time, the average aspect ratio was 4.3. A part of this pulverized product (15 kg) were sealed into a graphite crucible with a cover having an internal diameter of 40 cm and a volume of 40 l, the crucible was placed in an Acheson furnace and the powder was graphitized at a temperature of 2,800°C. The powder was left standing to cool and taken out to obtain 14 kg of powder. This powder was passed through a

270 mesh (53 μm) according to ASTM Standard to remove particles having a particle size of 53 μm or more. The properties of the graphite powder obtained are shown in Table 1.

[0021]

Comparative Example 1:

Coke A was sealed into a graphite crucible with a cover having an internal diameter of 40 cm and a volume of 40 ℓ , the crucible was placed in an Acheson furnace and the powder was graphitized at a temperature of 2,800°C. The powder was left standing to cool and taken out. Thereafter, the powder was coarsely pulverized in a pulverizer (manufactured by Hosokawamicron) into a size of from 2 to 3 mm or less. 15 kg of this coarsely pulverized product was finely pulverized in a jet mill (IDS2UR, manufactured by Nippon Neumatic). At this time, 95% of coarse particles having a particle size of 35 μm or more were continuously removed. The powder particles were then air-classified in a turbo-classifier (TC15N, manufactured by Nisshin Engineering) to remove 98% of particles having a particle size of 3 μm or less. At this time, the average aspect ratio was 5.1. This powder was passed through a 270 mesh (53 μm) according to ASTM Standard to remove particles having a particle size of 53 μm or more. The properties of the graphite powder obtained are shown in Table 1.

[0022]

Comparative Example 2:

Coke A was sealed into a graphite crucible with a cover having an internal diameter of 40 cm and a volume of 40 l, the crucible was placed in an Acheson furnace and the powder was graphitized at a temperature of 2,800°C. The powder was left standing to cool and taken out. Thereafter, the powder was coarsely pulverized in a pulverizer (manufactured by Hosokawamicron) into a size of from 2 to 3 mm or less. 15 kg of this coarsely pulverized product was finely pulverized in a jet mill (IDS2UR, manufactured by Nippon Neumatic). At this time, 95% of coarse particles having a particle size of 50 μ m or more were continuously removed. The powder particles were then air-classified in a turbo-classifier (TC15N, manufactured by Nisshin Engineering) to remove 98% of particles having a particle size of 8 μ m or less. At this time, the average aspect ratio was 4.9. This powder was passed through a 270 mesh (53 μ m) according to ASTM Standard to remove particles having a particle size of 53 μ m or more. The properties of the graphite powder obtained are shown in Table 1.

[0023]

Comparative Example 3:

Coke A was coarsely pulverized in a pulverizer (manufactured by Hosokawamicron) into a size of from 2 to 3

mm or less. This coarsely pulverized product was finely pulverized in a jet mill (IDS2UR, manufactured by Nippon Neumatic). At this time, 95% of coarse particles having a particle size of 10 μm or more were continuously removed. The powder particles were air-classified in a turbo-classifier (TC15N, manufactured by Nisshin Engineering) to remove 98% of particles having a particle size of 0.6 μm or less. At this time, the average aspect ratio was 4.5. A part of this pulverized product (15 kg) was sealed into a graphite crucible with a cover having an internal diameter of 40 cm and a volume of 40 ℓ , the crucible was placed in an Acheson furnace and the powder was graphitized at a temperature of 2,800°C. The powder was left standing to cool and taken out to obtain 14 kg of powder. This powder was passed through a 270 mesh (53 μm) according to ASTM Standard to remove particles having a particle size of 53 μm or more. The properties of the graphite powder obtained are shown in Table 1.

[0024]

Comparative Example 4:

Coke A was coarsely pulverized in a pulverizer (manufactured by Hosokawamicon) into a size of from 2 to 3 mm or less. This coarsely pulverized product was finely pulverized in a jet mill (IDS2UR, manufactured by Nippon Neumatic). At this time, 95% of coarse particles having a

particle size of 10 μm or more were continuously removed. The powder particles were air-classified in a turbo-classifier (TC15N, manufactured by Nisshin Engineering) to remove 98% of particles having a particle size of 0.6 μm or less. At this time, the average aspect ratio was 4.6. To a part of this pulverized product (14.4 kg), 0.6 kg of boron carbide (B_4C) was added and mixed in a Henschel mixer at 800 rpm for 5 minutes. The mixture powder was sealed into a graphite crucible with a cover having an internal diameter of 40 cm and a volume of 40 l, the crucible was placed in an Acheson furnace and the powder was graphitized at a temperature of 2,800°C. The powder was left standing to cool and taken out to obtain 14 kg of powder. This powder was passed through a 270 mesh (53 μm) according to ASTM Standard to remove particles having a particle size of 53 μm or more. The properties of the graphite powder obtained are shown in Table 1.

[0025]

Comparative Example 5:

Coke B was coarsely pulverized in a pulverizer (manufactured by Hosokawamicron) into a size of from 2 to 3 mm or less. This coarsely pulverized product was finely pulverized in a jet mill (IDS2UR, manufactured by Nippon Neumatic). At this time, 95% of coarse particles having a particle size of 50 μm or more were continuously removed.

The powder particles were air-classified in a turbo-classifier (TC15N, manufactured by Nisshin Engineering) to remove 98% of particles having a particle size of 8 μm or less. At this time, the average aspect ratio was 9.4. A part of this pulverized product (15 kg) was sealed into a graphite crucible with a cover having an internal diameter of 40 cm and a volume of 40 ℓ ; the crucible was placed in an Acheson furnace and the powder was graphitized at a temperature of 2,800°C. The powder was left standing to cool and taken out to obtain 14 kg of powder. This powder was passed through a 270 mesh (53 μm) according to ASTM Standard to remove particles having a particle size of 53 μm or more. The properties of the graphite powder obtained are shown in Table 1.

[0026]

Comparative Example 6:

Coke B was coarsely pulverized in a pulverizer (manufactured by Hosokawamicron) into a size of from 2 to 3 mm or less. This coarsely pulverized product was finely pulverized in a jet mill (IDS2UR, manufactured by Nippon Neumatic). At this time, 95% of coarse particles having a particle size of 50 μm or more were continuously removed. The powder particles were air-classified in a turbo-classifier (TC15N, manufactured by Nisshin Engineering) to remove 98% of particles having a particle size of 8 μm or

less. At this time, the average aspect ratio was 9.5. To a part of this pulverized product (14.4 kg), 0.6 kg of boron carbide (B_4C) was added and mixed in a Henschel mixer at 800 rpm for 5 minutes. The mixture powder was sealed into a graphite crucible with a cover having an internal diameter of 40 cm and a volume of 40 l, the crucible was placed in an Acheson furnace and the powder was graphitized at a temperature of 2,800°C. The powder was left standing to cool and taken out to obtain 14 kg of powder. This powder was passed through a 270 mesh (53 μm) according to ASTM Standard to remove particles having a particle size of 53 μm or more. The properties of the graphite powder obtained are shown in Table 1.

[0027]

Measurement of Battery Properties

The graphite powder having added thereto 3 wt% of polyvinylidene fluoride powder and N-methylpyrrolidone was kneaded and press-bonded to a copper mesh to form a negative electrode. For evaluating properties of this electrode as a single pole, a three-pole cell using lithium metal for the counter electrode and the reference electrode was manufactured.

The electrolytic solution used was a mixed solution of ethylene carbonate having dissolved therein 1 mol/l of $LiPF_6$ with dimethylene carbonate (1:1 by volume).

At the charging and discharging of the battery, the electric potential was controlled to 0.2 mA/cm² in both the charging and the discharging. The battery properties are shown in Table 1. In the table, the charge and discharge efficiency indicates a ratio of the electric capacity discharged to the electric capacity charged.

[0028]

[Table 1]

Example and Comparative Example No.	Average Particle Size (μm)	Specific surface Area (m^2/g)	Aspect Ratio	Tapping Density (g/cm^3)	5 μm or less, (wt%)	53 μm or more (wt%)	Lattice Spacing (Co. Value) (\AA)	B Content (wt%)	Discharge Capacity (mAh/g)	Initial Efficiency (%)
Example 1	11	2.54	4.1	0.98	1.7	0	6.733	0	310	80
" 2	21.4	1.71	4.1	1.1	0	0	6.74	0	281	87
" 3	20.6	1.34	4.1	1.0	0	0.2	6.717	4	335	91
" 4	15.9	2.98	4.5	0.91	1.7	0	6.734	0	286	87
Comparative Example 1	10.6	9.26	4.9	0.67	0.4	0.4	6.735	0	330	81
" 2	20.5	6.14	5.4	0.77	0	0	6.737	0	307	91
" 3	6.2	4.13	4.8	0.65	6.6	0	6.734	0	327	67
" 4	6.4	3.15	4.9	0.61	6	0	6.718	4	329	70
" 5	20.5	2.31	9.2	1.01	0	0	6.743	0	252	95
" 6	21.7	2.01	9.6	1.04	0	0	6.731	4	276	93
" 7	45.0	1.72	9.0	1.18	2.5	42	6.733	0	240	95

[0029]

[Effects of the Invention]

The graphite powder of the present invention has a small aspect ratio, accordingly, scaly particles are reduced. If the particle is scaly, the particles are oriented along the face of surface layer of the electrode, as a result, the permeability of electrolytic solution is deteriorated. The graphite powder particle of the present invention is nearly spherical and the permeability of electrolytic solution is good.

Due to small presence of scaly particles and by removing fine particles having a particle size of 3 μm or less, the bulk density of powder is high. The high bulk density means a high population of graphite particles per unit volume, accordingly, the intercalation ratio can be increased.

The graphite powder of the present invention has a small specific surface area because coke and the like are pulverized and then graphitized and fine particles and the like are removed, so that a passive film due to the electrolytic solution is not formed on the grain surface, the amount of binder used at the formation of an electrode can be reduced, and the contact between the graphite particle with the electrolytic solution is scarcely prevented by the binder.

Furthermore, by adding boron to the coke and the like powder and then graphitizing it, a high graphitization degree (crystallinity) can be attained and thereby the intercalation ratio of lithium into the graphite lattice can be elevated.

By virtue of these effects, the lithium battery using the graphite powder of the present invention for the negative electrode is advantageous in that the discharge capacity is large, the cycle property (battery life) is good, and the initial charge and discharge efficiency (discharge capacity to charge capacity of initial 1 to 3 times) is high.

[NAME OF THE DOCUMENT] Abstract

[SUMMARY]

[PROBLEM TO BE SOLVED]

To provide a carbon material for lithium battery having large discharge capacity, good cycle property and high charge and discharge efficiency.

[MEANS TO SOLVE THE PROBLEM]

To use graphite powder having a specific surface area of 3 m²/g or less, and aspect ratio of 6 or more and a tapping bulk density of 0.8 g/cm³ or more as the carbon material.

[SELECTED DRAWING] None.